

## Complete EOS for beta-HMX and Implications for Initiation

Ralph Menikoff, T-14

### Motivation

- Mesoscale simulations of initiation  
Resolve hotspots and use chemical reactions rather than coarse grain model
- Constitutive properties are input  
Need thermal and mechanical properties  
Need chemical reaction rates
- Estimates of phase space for initiation  
Check on compatibility of EOS and reaction rate  
Indication of physics that needs to be modeled

- Available EOS data

- Mechanical data

- Shock experiments

- Isothermal compression experiments

- Thermal data

- Specific heat

- Expansion coefficient

- Theoretical estimates

- Molecular dynamics

- Quantum chemistry

- Reaction rate

- Single Arrhenius rate from calorimetry experiments

- Multiple reactions fit to cook off experiments

- Tarver-McQuire three step model

- "Global chemical decomposition model"

- Henson et. al.

- Initiation

- Temperature on shock Hugoniot

- Multiple shocks for desensitization

- Estimates of **hotspot** temperature

- Dominant dissipative mechanism ?

- Growth mechanism for hotspots

- Deflagration ?

# Mechanical Data

## References

### **1. Isothermal data**

- Olinger, B., Roof, B. and Cady, H. (1978),  
The linear and volume compression of  $\beta$ -HMX and RDX,  
in *Proc. Symposium (Intern.) on High Dynamic Pressures*,  
[C.E.A., Paris, France], pp. 3–8.
- Yoo, C.-S. and Cynn, H. (1999),  
Equation of state, phase transition, decomposition of  $\beta$ -HMX,  
*J. Chem. Phys.* **111**, pp. 10229–10235.

Menikoff & Sewell (2001),  
Fitting Forms for Isothermal Data,  
*High Pressure Research* **21** pp. 121-138.

<http://t14web.lanl.gov/Staff/rsm/preprints.html#IsothermFit>

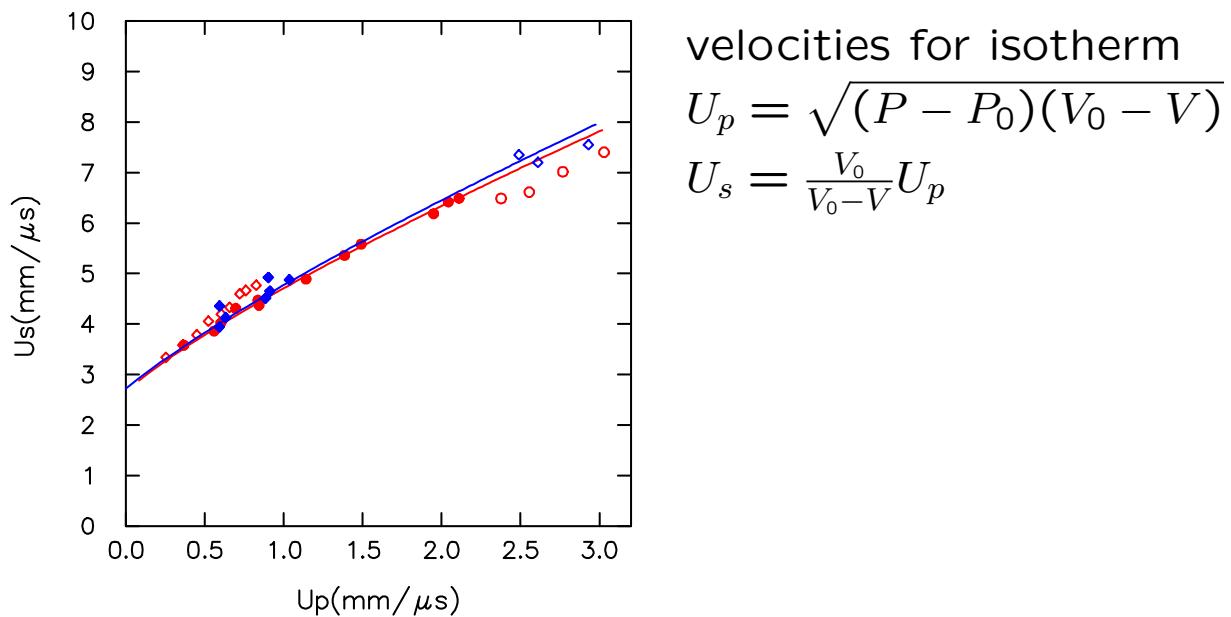
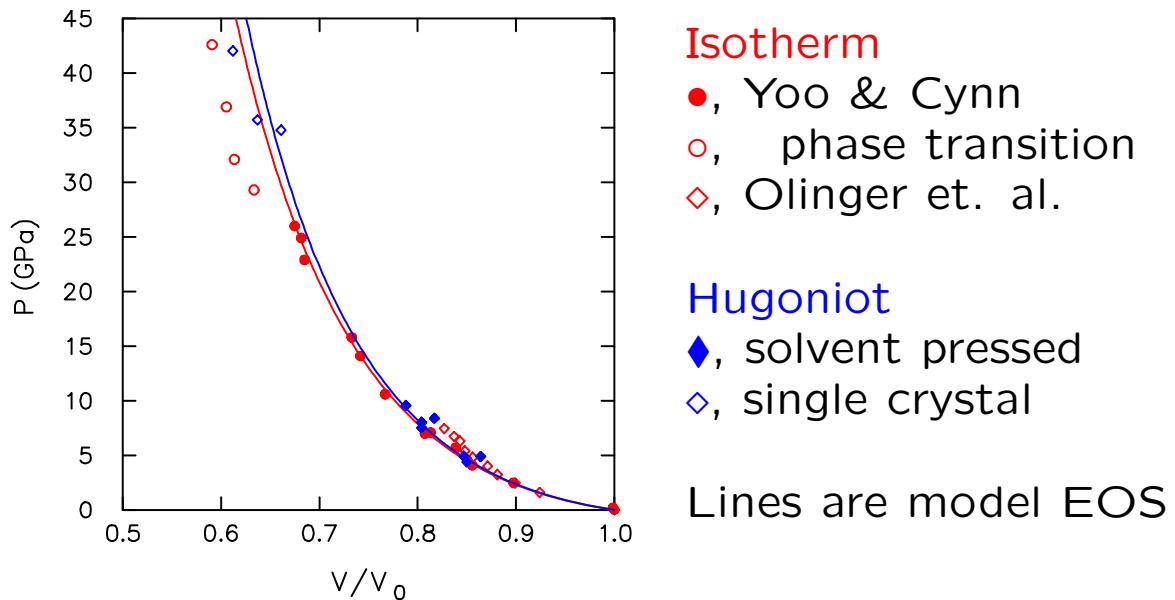
### **2. Hugoniot data**

- S. Marsh, ed. (1980),  
*LASL Shock Hugoniot Data*, [Univ. Calif. press].

<http://lib-www.lanl.gov/ladcdmp/shd.pdf>

- Craig, R. G. (1974),  
Data from shock initiation experiments,  
[Technical Report M-3-QR-74-1, Los Alamos Scientific Lab.].  
Alternatively,  
Travis & Campbell, 8th Symposium on Detonation.  
Mader, Numerical Modeling of Explosives and Propellants, p. 218.

## Mechanical Data



# Thermal Data

## References

### 1. Specific heat

Koshigoe, L. G., Shoemaker, R. L., and Taylor, R. E. (1984),  
Specific Heat of HMX,  
*AIAA Journal*, **22**, pp. 1600–1601.

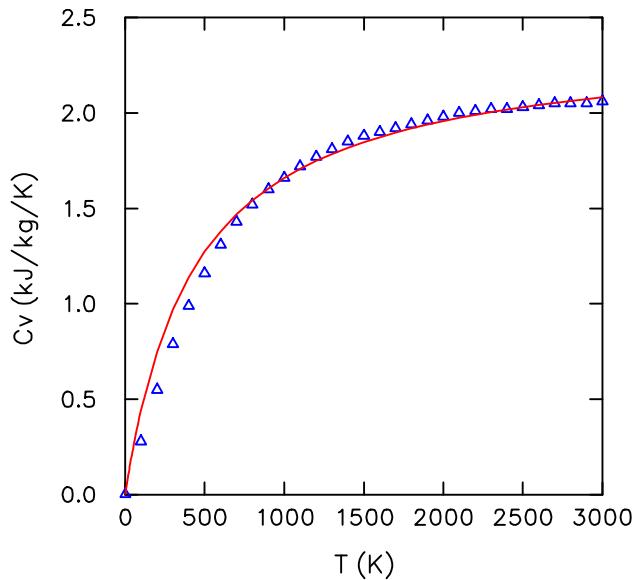
W. A. Goddard et. al. (1998),  
*Center for Simulation of Dynamic Response in Materials Annual Technical Report 032*, Fig. 4.16 on p. 96.

<http://www.galcit.caltech.edu/~jeshep/asci/www/reports.html>

### 2. Thermal expansion

Herrmann, H., Engel, W., and Eisenreich, N. (1993),  
Thermal analysis of the phases of HMX using X-ray diffraction,  
*Zeitschrift für Kristallographie*, **204**, pp. 121–128.

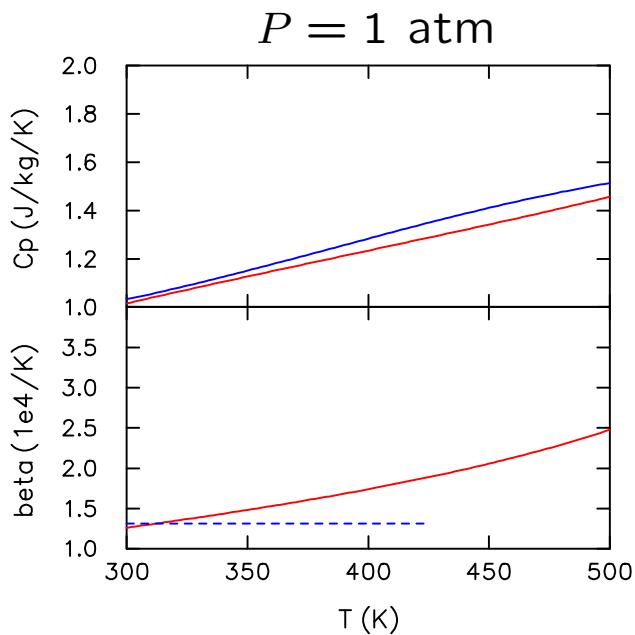
## Thermal Data



$$C_V = \frac{\partial e}{\partial T} \Big|_V$$

symbols

Goddard et. al.  
molecular dynamics  
line is fit  
model EOS



$$C_P = \frac{\partial(e + PV)}{\partial T} \Big|_P$$

line experiment  
line model EOS

$$\beta = \frac{1}{V} \frac{\partial V}{\partial T} \Big|_P$$

Thermal expansion  
Highly anisotropic

## Free Energy for Complete EOS

$$F(V, T) = \underbrace{- \int_{V_0}^V dV P_0(V)}_{\text{cold curve}} - \underbrace{\theta(V) \int_0^{T/\theta} \frac{d\tilde{T}}{\tilde{T}} \left( \frac{T}{\theta} - \tilde{T} \right) \hat{C}_V(\tilde{T})}_{\text{thermal component}}$$

where Birch-Murnaghan form for  $T = 0$  isotherm

$$P_0(V) = \frac{3}{2} K_0 \left( \eta^{-7/3} - \eta^{-5/3} \right) \left[ 1 + \frac{3}{4} (K'_0 - 4) (\eta^{-2/3} - 1) \right]$$

$\eta = V/V_0$ , compression ratio

$K_0$  = isothermal bulk modulus at  $T = 0$  and  $V = V_0$

$$K'_0 = \left. \frac{dK_{T=0}}{dP} \right|_{V=V_0}$$

Specific heat of form  $C_V(V, T) = \hat{C}_V(T/\theta(V))$

$$\hat{C}_V(\tilde{T}) = \frac{\tilde{T}^3}{c_0 + c_1 \tilde{T}^2 + c_2 \tilde{T}^2 + c_3 \tilde{T}^3}$$

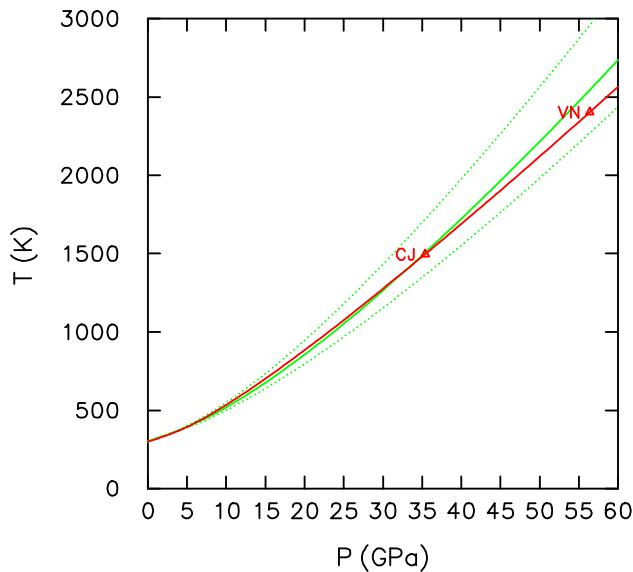
“Debye temperature”

$$\theta(V) = \theta_0 \left( \frac{V_0}{V} \right)^a \exp[b(V_0 - V)/V]$$

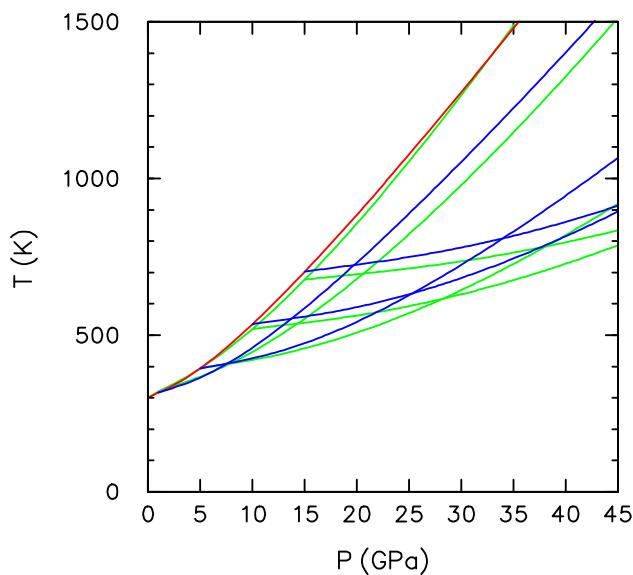
gives Grüneisen coefficient

$$\Gamma(V) = -\frac{V}{\theta} \frac{d\theta}{dV} = a + b \frac{V}{V_0}$$

## Temperature on Shock Loci



model EOS  
CJ – CJ pressure  
VN – von Neumann spike  
Mie-Grüneisen  
 $C_V$  constant  
solid – best fit  
dotted – sensitivity



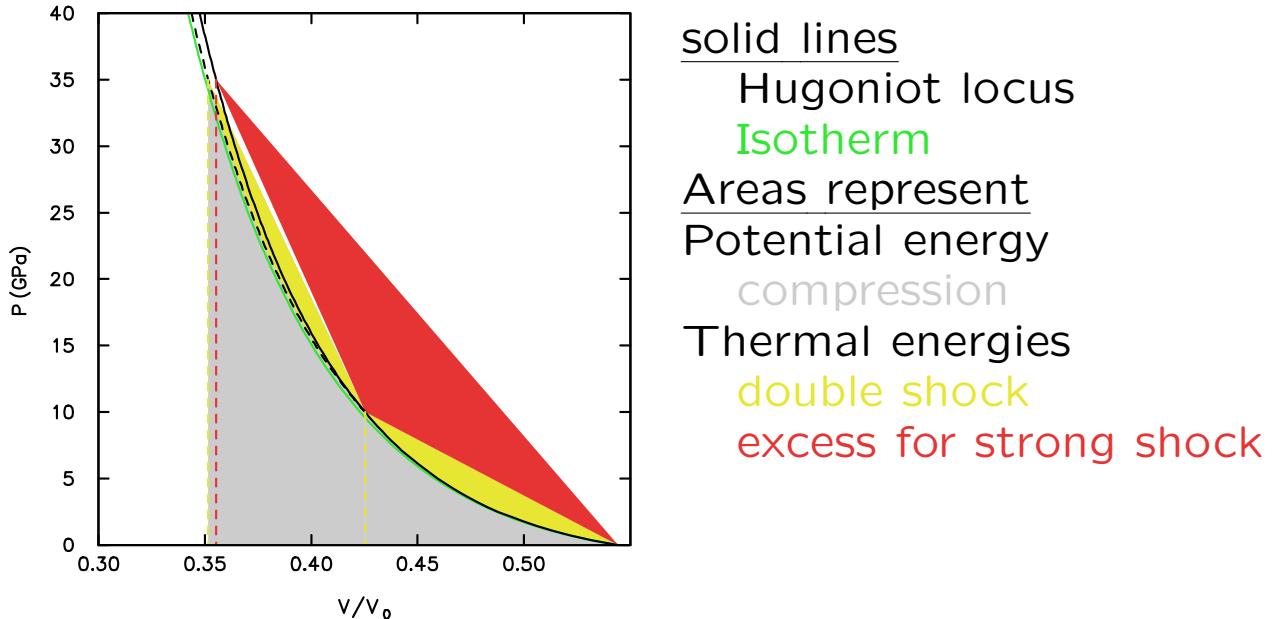
principle Hugoniot  
second shock  
Mie-Grüneisen

Temperature of double shock less than single shock  
Key factor in shock desensitization

## Shock Heating

Compare single shock to same pressure as two weaker shocks

### Geometric Interpretation



Shock energy (Hugoniot equation)

$$e_1 - e_0 = \frac{1}{2}(P_1 + P_0)(V_0 - V_1)$$

Energy on cold curve

$$e_c(T) = - \int_{V_0}^{V_1} P_{T=0}(V) dV$$

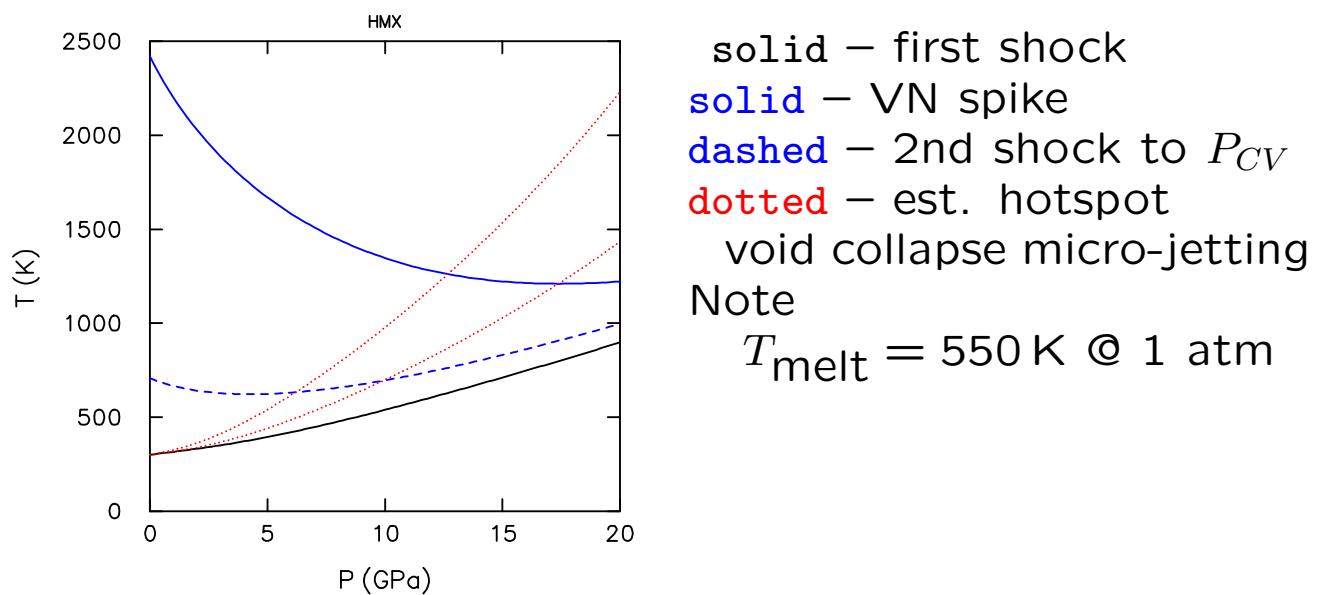
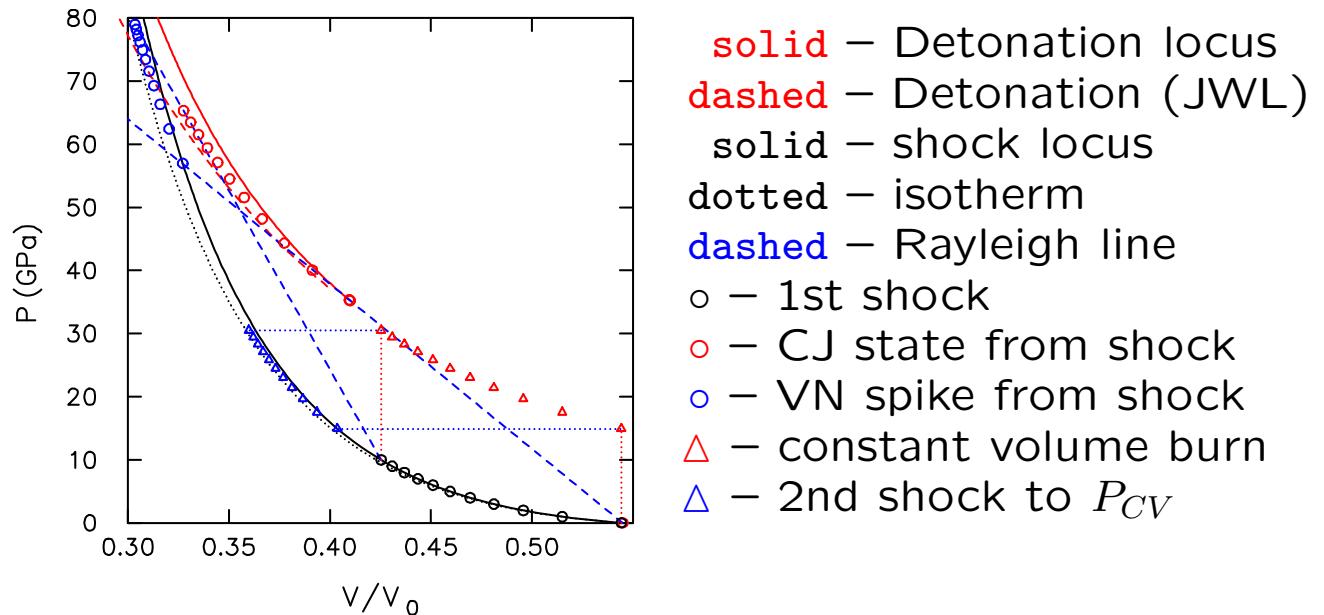
Thermal energy

$$e_{\text{thermal}} = \int_{T_0}^{T_1} C_V(T) dT$$

## Detonation Locus

References: Product EOS

Fritz et al. J. Appl. Phys. **80** (1996) pp. 6129–6141  
 Hixon et al. J. Appl. Phys. **88** (2000) pp. 6287–6293

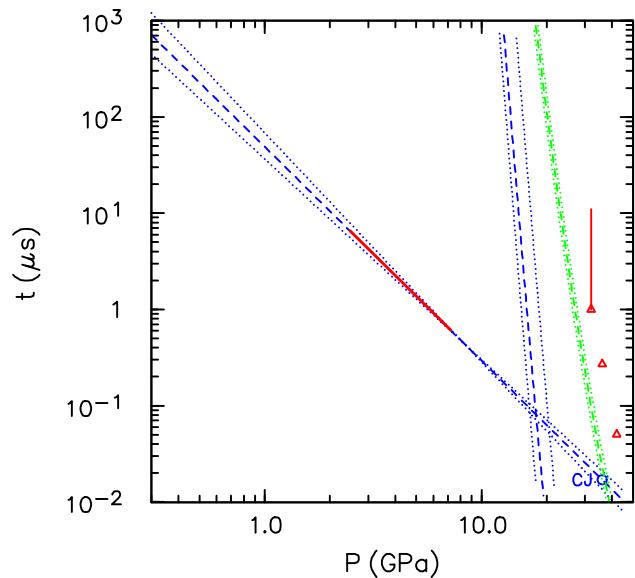


## Reaction Rates

### References

1. Gibbs & Popolato (1980),  
LASL Explosive Properties  
<http://lib-www.lanl.gov/ladcdmp/epro.pdf>  
Pop plot data  
Arrhenius parameters (R. Rodgers)
2. Henson, B. F., Asay, B. W., Smilowitz, L. B. and Dickson, P. M. (2001),  
Ignition Chemistry in HMX from Thermal Explosion to Detonation  
*Proc. Shock Compression of Condensed Matter – 2001*
3. McQuire, R. R. and Tarver, C. M. (1981),  
Chemical Decomposition Models for the Thermal Explosion Con-  
fined HMX, TATB, RDX and TNT Explosives,  
*Seventh Symposium on Detonation*
4. Craig, R. G. (1974),  
Data from shock initiation experiments,  
[Technical Report M-3-QR-74-1, Los Alamos Scientific Lab.].  
Alternatively,  
Travis & Campbell, 8th Symposium on Detonation.  
Mader, Numerical Modeling of Explosives and Propellants, p. 218.

## Reaction Rates

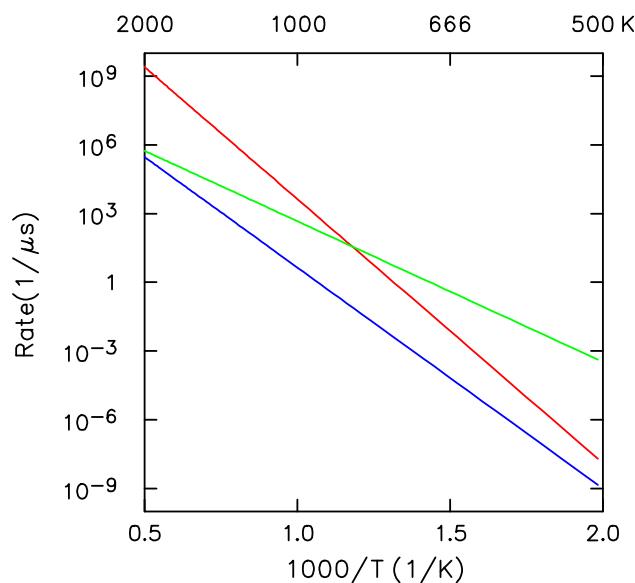


PBX-9501

**solid** – Pop plot data  
**dashed** – “Global model”

HMX

**dashed** – Arrhenius rate  
**△** single crystal wedge exp.



Tarver-McQuire 3-step

**solid** – endothermic

$Q/C_p \approx 200^\circ\text{K}$

**solid** – exothermic  
 small energy release  
 Rate limiting step

**solid** – exothermic  
 large energy release

cookoff regime

$T \approx 500\text{ K}$

## Comments

- $500 < T < 800 \text{ K}$

Phase transition important

either  $\beta \rightarrow \delta$  or melting

$L/C_V \approx 200 \text{ K}$

$\Delta V/V \approx 10\%$

Need to incorporate phase transition in EOS

- High temperatures,  $T \gtrsim 2000 \text{ K}$

(von Neumann spike temperature)

Standard rates for HMX are too large

Conjecture – pressure dependence to rate

from high density limits mobility of atoms

- Growth of Hotspots

$\Delta T$  from pressure wave too low

Growth from deflagration controlled by

Thermal conductivity & surface area

Estimated regression rate too low

Resolution problem for mesoscale simulations

Critical question for modeling